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6. AUTHOR(S)
Lawrence K. Montgomery

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Indiana University/Bryan Hall
PO Box 1847
Bloomington, IN 47402-1847

8. PERFORMING ORGANIZATION REPORT NUMBER

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13. ABSTRACT (Maximum 200 words)

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Design and Synthesis of Organic Superconductors

Lawrence K. Montgomery (PI)
Department of Chemistry
Indiana University
Bloomington, IN 47405

31 August 1996

ABSTRACT

The principal objectives of this work were the design, synthesis, and preliminary characterization of new organic conductors and superconductors. Electrocrystallization facilities were constructed that accommodate 96 crystal growth cells. Crystal formation takes place in a temperature-controlled (±0.1 C), vibrationally-isolated, (vertical isolation efficiency at 10 Hz in 60-90%), inert-atmosphere environment. A variety of radical-cation salts of bis(ethylenedithio)tetraselenafulvalene were grown and characterized by crystallography, tight-binding band calculations, electronic transport, magnetic properties, and a number of other solid-state methods. Significant findings include the discovery of a tetrachlorogallate salt that is a superconductor with a transition temperature 5.5° higher than any previously known organic material containing selenium and magnetoresistance studies on mercury thiocyanate salts that suggest that strong electron-electron interactions are important in promoting and enhancing superconductivity in organic superconductors. A new organic conductor precursor, bis(ethylenedithio)tetrathiohaphthalene, was synthesized and several of its conducting salts were investigated in a preliminary manner. Numerous collaborative studies were undertaken.

RESEARCH SUMMARY

A. Facilities Development.

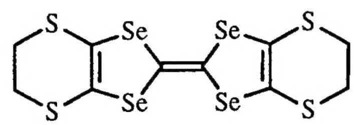
With the aid of the departmental electronics, computer, and mechanical services groups, crystal growth facilities were constructed that accommodate 96 electrocrystallization cells. The cells are housed in 150-lb. thermostated (25-80°C, ±0.1°C) boxes (12 cells per box, dry nitrogen or argon available) constructed of angle iron and chip board and lined with acoustical foam composite. Each box rests on a Technical Manufacturing Corporation Series 64 table-top vibration isolation system (vertical isolation efficiency @ 10 Hz: 60-90%). A 96-cell constant current/voltage (0-40.95 μA/0-10.23 volts) system that was designed by the department's

electronics group and is computer controlled. It has a back-up computer and emergency power sources. The electrical history of each cell is available on a monitor and is routinely recorded for each experiment. To our knowledge, this is the premier electrocrystallization facility in the United States.

A Vacuum Atmospheres Glove Box was equipped with six vibrationally-isolated electrocrystallization cells. The glove box was used for growing and handling air-sensitive materials. A helium refrigerator system was designed in collaboration with the of RMC Corporation for resistance measurements that maintains highly stable temperatures to below 10 K. It has a double sample holder that is particularly useful for comparative measurements and isotope effect studies. The helium refrigerator apparatus was one of our primary instruments for screening new crystals. Additionally, AC and DC resistance measurements and AC susceptibility measurements were made to 2.3 K with a Lakeshore Model 7110 helium cryostat system.

B. Radical-Cation Based Conductors.

1. Bis(ethylenedithio)tetraselenafulvalene, BEDT-TSF or BETS (1). Our interest in BETS-based conductors arose from a comparison of the similarities and differences



1

BEDT-TSF or BETS

between the organic radical-cation superconductors with T_c's over 10 K and the high-T_c cuprate superconductors.[1]

A multistep synthesis of BETS was outlined in 1983.[2] Since a number of factors suggested that the reported BETS synthesis was less than ideal, our initial efforts focused on an improved preparation of BETS starting from tetraselenafulvalene.[3] An alternative route to BETS was published while this work was in progress.[4]

In preparing radical-cation salts of BETS, our emphasis was on systems that are isostructural with known ET superconductors (*e.g.*, κ-$(BETS)_2Cu[N(CN)_2]X$ where X = Br[5] and Cl,[6] κ-$(BETS)_2Cu[NCS]_2$,[7] and β-$(BETS)_2I_3$).[8] Because of the very limited solubility of BETS in typical electrocrystallization solvents, the preparation of BETS salts was attempted at elevated

(40-55°C) temperatures. This modest change in reaction conditions greatly facilitated the synthesis of BETS conductors. Several solvents were screened for electrocrystallization (1,1,2-trichloroethane (TCE), TCE-ethanol mixtures, 1,1,1-trichloroethane (1,1,1-TCE), TCE:1,1,1-TCE mixtures, chlorobenzene, and benzonitrile). TCE-ethanol proved to be one of the most useful solvents. Over two dozen salts were screened: $Cu[N(CN)_2]X^-$ where X^- = Cl, Br, I; $Cu(NCS)_2^-$, $GaCl_4^-$, SbF_6^-, $CF_3SO_3^-$, $CH_3SO_3^-$, NO_3^-, I_3^-, IBr_2^-, $AuCl_4^-$, $GaBr_4^-$, $TlCl_4^-$, $TlBr_4^-$, TlI_4^-, $TlI_4(I_3)^-$, $FeCl_4^-$, $FeBr_4^-$, $InBr_4^-$, InI_4^-, Hg_3I_8, $KHg(SCN)_4$, and $NH_4Hg(SCN)_4)$[3,9,10,11]. Multiple stoichiometries and crystal packing motifs were observed for several of the anions. Many of the salts were characterized in detail [X-ray structures at 100 K and 300 K, resistivity measurements from 300 K to 15 K (some to 2 K), AC susceptibility from 300 K to 4 K (some to 0.2 K with RF penetration depth measurements),[3,9,10,11] tight-binding band calculations, and pressure studies at 4 K (0.5-5 kbar)]. More detailed measurements (critical field, magnetoresistance, magnetization studies) were carried out on a few systems in collaboration with several physics research groups (listed in parentheses).

As a class, the BETS conductors are quite interesting; many are metallic (resistivity decreases with temperature) at room temperature and remain so to at least 10-15 K. κ- and θ-phases, which have yielded the ET superconductors with the highest T_c's, abound. No κ- or θ-phases were superconducting, however.

We succeeded in preparing κ-$(BETS)_2Cu[N(CN)_2]Br$,[9] which is isostructural (300 K, 95 K, and 20 K) with the radical-cation superconductor κ-$(ET)_2Cu[N(CN)_2]Br$ (T_c = 11.6 K).[5] The resistivity of κ-$(BETS)_2Cu[N(CN)_2]Br$ decreases monotonically from 300-4 K, but a superconducting state is never achieved.[1] Complementary RF penetration depth measurements (~500 kHz) failed to detect superconductivity at 0.5 K (J. M. Williams and G. W. Crabtree). Structurally, the most significant difference between κ-$(BETS)_2Cu[N(CN)_2]Br$ and κ-$(ET)_2Cu[N(CN)_2]Br$ is that one of the ethylenedithio groups of the BETS component is disordered to at least 20 K (C. E. Strouse and S. I. Khan). It is likely that this disorder is responsible for the lack of superconductivity in K-$(BETS)_2Cu[N(CN)_2]Br$. Pressure (0.5-5 kbar at 4K) does not induce superconductivity (J. E. Schirber).

Our most significant finding to date is the discovery of superconductivity in λ-$(BETS)_2GaCl_4$.[10] We reported the synthesis and resistivity profile of κ-$(BETS)_2GaCl_4$ in 1992.[3] A relatively sharp resistive transition is observed in the λ-phase material with an onset of about 7.5 K, a midpoint of 6 K, and negligible resistivity below 5 K. Superconductivity was confirmed by AC susceptibility (onset 5.1 K, midpoint 4.5 K, ΔT = 1 K). X-ray crystal structures

($P\bar{1}$) at 300 and 100 K show that the BETS dimers (nonequivalent BETS molecules) pack in a zig-zag fashion (denoted λ) in the ac-plane in layers, alternating with $GaCl_4^-$ layers. Pressure measurements (J. E. Schirber) have demonstrated a negative pressure effect on T_c ($dT_c/dP \sim -0.3$ K/kbar). Several samples had much broader resistive transitions with higher onsets (>9 K). It was also found that the application of gold paste can raise the onset of superconductivity as measured by AC susceptibility by several degrees. The effect is reversible (onset, sharpness), but the final absolute susceptibility after removing the gold paste is lowered somewhat. These interesting observations are being examined further. Tight-binding band calculations (M.-H. Whangbo) suggest that λ-$(BETS)_2GaCl_4$ has both 1-D and 2-D Fermi surfaces, the most prominent feature being a closed hole pocket centered at X accounting for ~33% of the first Brillouin zone. STM and AFM measurements on λ-$(BETS)_2GaCl_4$ have been completed (S. N. Maganov) and the results are being compared with theoretical electron density calculations (M.-H. Whangbo).

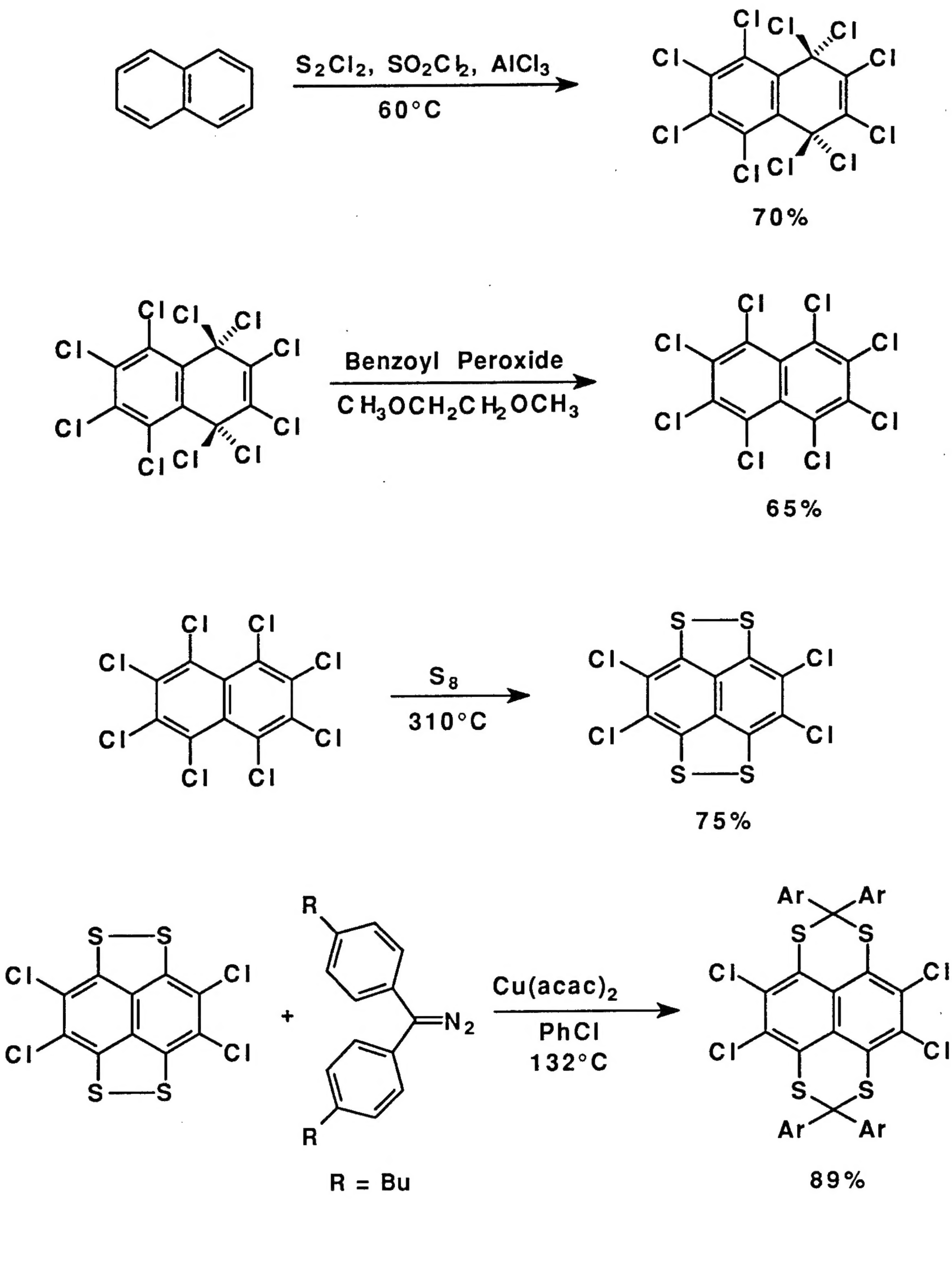
The discovery of superconductivity in λ-$(BETS)_2GaCl_4$ is noteworthy from several points of view. It is the first superconductor derived from BETS. The onset of superconductivity at 7.5 K is 5.5° higher than any other organic superconductor containing selenium.[12] There are only four other radical-cation based superconductors that have higher T_c's than λ-$(BETS)_2GaCl_4$.[12] Kobayashi and coworkers have published resistivity data and a room temperature crystal structure of λ-$(BETS)_2GaCl_4$.[13] Their results are in complete experimental agreement with our work.

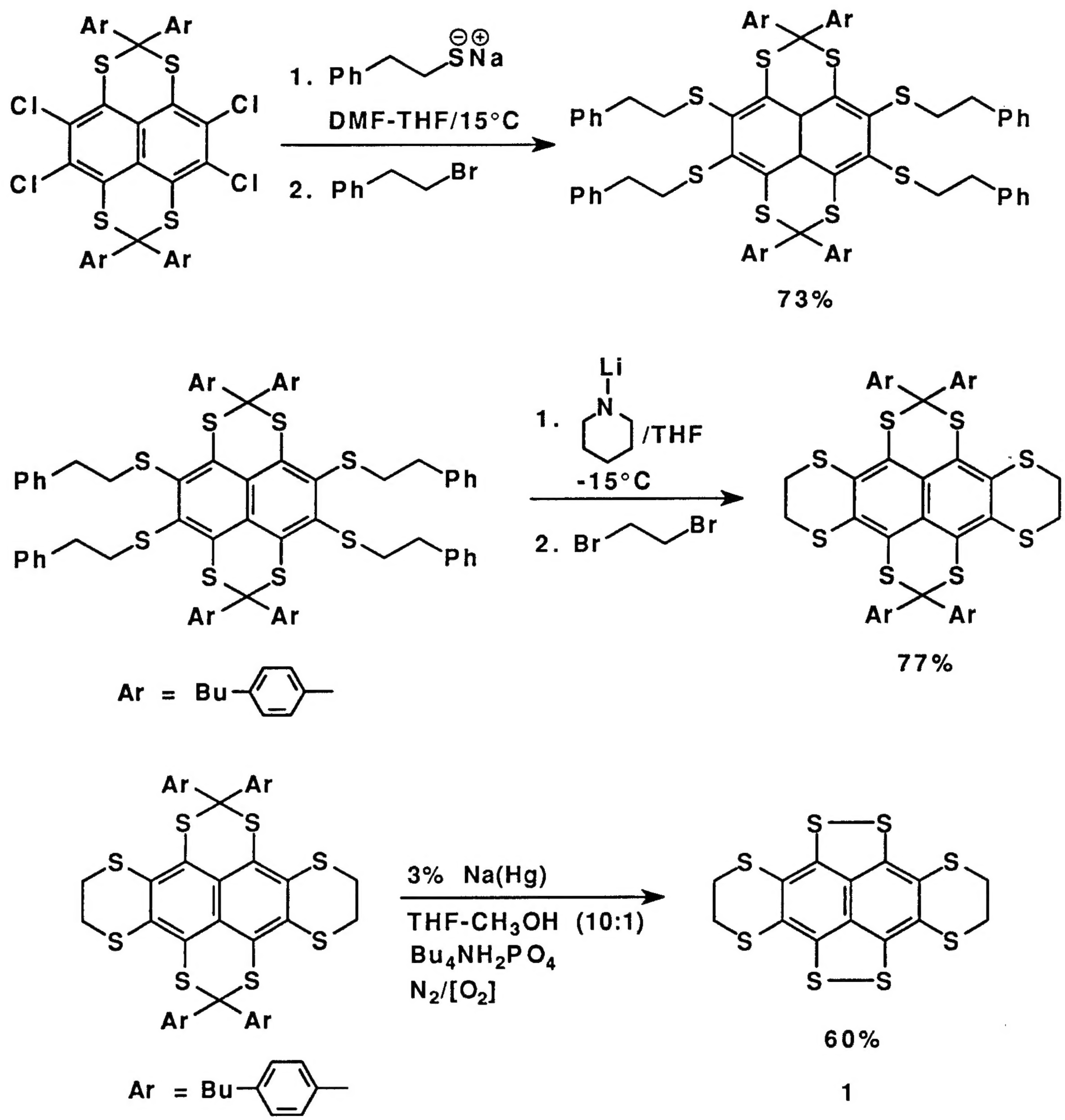
The vortex dynamics and pinning parameter, α, have been examined recently for λ-$(BETS)_2GaCl_4$ (C. C. Agosta). The pinning parameter is 44 N/m^2, almost three orders of magnitude less than the layered cuprate superconductor YBCO. It is readily conceivable that pinning studies like this on organic superconductors might be of considerable value in understanding pinning phenomena in the copper oxide superconductors.[14]

In an attempt to understand the variable T_c's in λ-$(BETS)_2GaCl_4$, nine different crystal morphologies we isolated from the electrocrystallization products of BETS and tetrabutylammonium tetrachlorogallate.[15] The morphologies were examined by X-ray crystallography and electrical transport measurements and have been assigned to several different crystal systems: κ-, λ-, and κ'-$(BETS)_2GaCl_4$, α-$(BETS)_3GaCl_4$•TCE, and an incompletely characterized semiconductor. Anisotropic pressure studies are continuing on this system (J. S. Brooks).

Two BETS salts, α-$(BETS)_2MHg(SCN)_4$ (M = NH_4 and K), were prepared that are isostructural with the BEDT-TTF compounds α-$(BEDT\text{-}TTF)_2MHg(SCN)_4$ (M = NH_4 and K).[16] α-$(BEDT\text{-}TTF)_2NH_4Hg(SCN)_4$ is a superconductor (T_c = 1.1K); α-$(BEDT\text{-}TTF)_2KHg(SCN)_4$ is metallic to at least 50mK but is not a superconductor. Both BETS compounds are metallic to at least 0.4K but neither exhibit superconductivity. Tight-binding band calculations were published comparing the BEDT-TTF and BEDT-TSF systems (M.-H. Whangbo).[17] The calculations suggest some interesting differences in the Fermi surfaces of the BEDT-TTF and BEDT-TSF (BETS) systems, that should be possible to verify experimentally employing angle-dependent magnetoresistance studies. Such experiments are in progress (J. S. Brooks). Simple magnetoresistance studies on α-$(BETS)MHg(SCN)_4$ (M = NH_4 and K) have been completed (C. C. Agosta).[18] Cyclotron resonance studies are also being performed on the BETS salts (J. Singleton). The results of these studies to date suggest that strong electron-electron interactions are important in promoting and enhancing superconductivity and enhancing superconductivity in organic superconductors. Electron-electron interactions are greatly reduced in BETS compounds compared to their isostructural ET relatives.

A. Bis(ethylenedithio)tetrathionaphthalene (BEDT-TTN) 1). Recently, the synthesis of the potential organic superconductor precursor, BEDT-TTN, was achieved. The seven step synthesis is shown below.


S2Cl2, SO2Cl2, AlCl3
60°C
70%
Benzoyl Peroxide
CH3OCH2CH2OCH3
65%
S8
310°C
75%
Cu(acac)2
PhCl
132°C
R = Bu
89%



All of the steps proceed in 60-89% yields, and optimization of the reaction conditions is continuing.

Over a dozen radical cation salts of BEDT-TTN were prepared by electrocrystallization. Three salts, (BEDT-TTN) ClO_4, (BEDT-TTN)$_3$(SCN)$_2$, and (BEDT-TTN)$_2$I$_3$, were characterized by four-probe electrical transport measurements, ESR spectroscopy, and X-ray crystallography. The 1:1 ClO_4 salt is a semiconductor [E_a = 262(15) meV (323-270 K)] as expected. (BEDT-TTN)$_3$(SNC)$_2$'s room temperature conductivity is six orders of magnitude

greater than that of (BEDT-TTN)ClO_4, but it is also a semiconductor [E_a = 93(7) meV (290-180 K), E_a = 62(6) meV (180-70 K)]. The first metallic system is (BEDT-TTN)$_2I_3$ [T_{MI} = 170 K, E_a = 88(4) MEV (170-90 K)].

C. Collaborations.

In addition to the collaborations noted in sections **A** and **B** (affiliations noted below), three manuscripts on organic conductors and superconductors were published with Professor Joseph Brill.

1. AC Calorimetry at Charge Density Wave (CDW) and Spin Density Wave (SDW) Transitions.[19]

The specific heats at the SDW transition in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl and the CDW transition in (TMTSF)$_2ReO_4$ have been measured. No anomaly is observed in the SDW transition. For (TMTSF)$_2ReO_4$ there is a sample-dependent latent heat associated with anion ordering.

2. Electric Field Dependence of Young's Modulul of (TMTSF)$_2PF_6$.[20]

The Young's modulus (Y) and internal friction (1/Q) in (TMFTSF)$_2PF_6$ have measured at 5.5K as functions of electric field. No changes ($\Delta Y/Y$, $\Delta 1/Q < 2 \times 10^{-4}$) are observed at fields up to 100 E_T, the threshhold for SDW depinning, in contrast to what is observed for many sliding CDW materials. A possible explanation is that bulk depinning of the SDW is not observed.

3. Thermodynamics of the Anion Ordering Transitions in (TMTSF)$_2ReO_4$ and (TMTSF)$_2BF_4$.[21] The heat capacities were measured by AC calorimetry.

Major collaborators in this grant and their affiliations were:

J. W. Brill, Department of Physics, University of Kentucky

M.-H. Whangbo, Department of Chemistry, North Carolina State University

J. E. Schirber (retired), Sandia National Laboratory

J. M. Williams and G. W. Crabtree, Divisions of Chemistry and Materials Science, Argonne National Laboratory.

C. C. Agosta, Physics Department, Clark University

J. S. Brooks, NHMFL, Department of Physics, Florida State University

S. N. Magonov, Materials Research Center, Albert-Ludwigs University, Germany

C. E. Strouse and S. I. Khan, Department of Chemistry, University of California, Los Angeles

J. Singleton, Clarendon Laboratories, University of Oxford, United Kingdom

REFERENCES

1. T. Burgin, T. Miebach, J. C. Huffman, L. K. Montgomery, J. A. Paradis, C. Rovira, M.-H. Whangbo, S. N. Magonov, S. I. Khan, C. E. Strouse, D. L. Overmyer and J. E. Schirber, "20 K Crystal Structure, Electrical Transport, Electronic Band Structure, Scanning Tunnelling Microscopy and Pressure-RF Impedance Studies on the Organic Conducting Salt κ-$(BEDT\text{-}TSF)_2Cu[N(CN)_2]Br$," J. Mater. Chem., *5 (10)*, 1659 (1995).

2. R. R. Schumaker, V. Y. Lee, E. M. Engler, J. Phys. Colloq. (France) **1983**, *C3*, 1139.

3. L. K. Montgomery, T. Burgin, C. Husting, L. Tilley, J. C. Huffman, K. D. Carlson, J. D. Dudek, G. A. Yaconi, U. Geiser, J. M. Williams, Mol. Cryst. Liq. Cryst. **1992**, *211*, 283.

4. R. Kato, H. Kobayashi, A. Kobayashi, Synth. Met. **1991**, *41*, 2093.

5. A. M. Kini, U. Geiser, H. H. Wang, K. D. Carlson, J. M. Williams, W. K. Kwok, K. G. Vandervoort, J. E. Thompson, D. Stupka, D. Jung, M.-H. Whangbo, Inorg. Chem. **1990**, *29*, 2555.

6. J. M. Williams, A. M. Kini, H. H. Wang, K. D. Carlson, U. Geiser, L. K. Montgomery, G. J. Pyrka, D. M. Watkins, J. M. Kommers, S. J. Boryschuk, A. V. Strieby Crouch, W. K. Kwok, Inorg. Chem. **1990**, *29*, 3272.

7. H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto, J. Tanaka, J. J. Chem. Lett. **1988**, 55.

8. R. B. Yagubskii, I. F. Shchegolev, V. N. Laukhin, P. A. Kononovich, M. W. Karatsovnik, A. V. Zvarykina, L. I. Buravov, Pis`ma Zh. Eksp. Teor. Fiz. **1984**, *39*, 12; JETP Lett. (Engl. Transl.) **1984**, *39*, 12.

9. L.K. Montgomery, T. Burgin, J. C. Huffman, K. D. Carlson, J. D. Dudek, G. A. Yaconi, L. A. Megna, P. R. Mobley, W. K. Kwok, J. M. Williams, J. E. Schirber, D. L. Overmyer, J. Ren, C. Rovira, M.-H. Whangbo, Synth. Met., **1993**, *56*, 2090.

10. L. K. Montgomery, T. Burgin, J. C. Huffman, J. Ren, M.-H. Whangbo, Physica C **1994**, *219*, 490.

11. L. K. Montgomery, B. W. Fravel, J. C. Huffman, C. C. Agosta, and S. A. Ivanov, "Synthesis and Preliminary Characterization of New Conducting Salts Derived from Bis(ethylenedithio)tetraselenafulvalene (BETS)," Synth. Met., *85*, in press.

12. J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, M.-H. Whangbo, Organic Superconductors (Including Fullerenes); Prentice Hall: Englewood Cliffs, NJ, 1992; Chapt 1.

13. H. Kobayashi, T. Udagawa, H. Tomita, K. Bun, T. Naito, A. Kobayashi, Chem. Lett. **1993**, 1559.

14. C. H. Mielke, Ph.D. thesis, Clark University, 1996.

15. L. K. Montgomery, T. Burgin, T. Miebach, D. Dunham, and J. C. Huffman, "Characterization of the Electrocrystallization Products of Bis(ethylenedithio)tetra-selenafulvalene (BETS) and Tetrabutylammonium Tetrachlorogallate," Mol. Cryst. Liq. Cryst., *284*, 73 (1996).

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17. D.-K. Seo, M.-H. Whangbo, B. W. Fravel, and L. K. Montgomery, "Comparison of the Fermi Surfaces of Isostructural Organic Conducting Salts (BEDT-TTF)$MHg(SCN)_4$ and $(BEDT\text{-}TSF)_2MHg(SCN)_4$ ($M = NH_4$ and K), Solid State Commun., *100*, 191 (1996).

18. S. A. Ivanov, C. H. Mielke, T. Coffey, D. A. Howe, C. C. Agosta, B. W. Fravel, and L. K. Montgomery, "Electronic-Transport Studies of the Organic Metals α-$(BETS)_2NH_4Hg$-$(SCN)_4$ and α-$(BETS)_2KHg(SCN)_4$ in High Magnetic Fields, Phys. Rev. B. Condens. Matter, *55*, 1829 (1996).

19. M. Chung, Y. Wang, J.W. Brill, T. Burgin, and L.K. Montgomery, "AC Calorimetry at CDW and SDW Transitions," Synth. Met., *56*, 2755 (1993).

20. Z.G. Xu, G. Minton, J.W. Brill, T. Burgin, and L.K. Montgomery, "Electric Field Dependence of Young's Modulus of $(TMTSF)_2PF_6$," Synth. Met., *56*, 2797 (1993).

21. M. Chung, T. Burgin, E. Figueroa, Y.-K. Kuo, Y. Wang, L. K. Montgomery, and J. W. Brill, "Thermodynamics of the Anion Ordering Transitions in $(TMTSF)_2ReO_4$ and $(TMTSF)_2BF_4$," Phys. Rev. B.: Condens. Matter, *48*, 9256 (1993).

COMPLETED PROJECT SUMMARY

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INCLUSIVE DATES: 30 Sept 1992 - 30 June 1996

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SENIOR RESEARCH PERSONNEL: Dr. Steven Kaganove
Dr. Thomas Miebach

JUNIOR RESEARCH PERSONNEL: Graduate Students
Timothy P. Burgin (Ph.D., 1994)
John J. Becker (M.S., 1995)
Kyle P. Starkey
Bradley W. Fravel
Heather Peterson

Technical
Sheryl Lifer

Undergraduates
Christopher Gerst
Dennis Dunham
Timothy Martin

PUBLICATIONS:

1. L. K. Montgomery, B. W. Fravel, J. C. Huffman, C. C. Agosta, and S. A. Ivanov, "Synthesis and Preliminary Characterization of New Conducting Salts Derived from Bis(ethylenedithio)tetraselenafulvalene (BETS)," Synth. Met., *85*, in press.

2. S. A. Ivanov, C. H. Mielke, T. Coffey, D. A. Howe, C. C. Agosta, B. W. Fravel, and L. K. Montgomery, "Electronic-Transport Studies of the Organic Metals α-$(BETS)_2NH_4Hg$-$(SCN)_4$ and α-$(BETS)_2KHg(SCN)_4$ in High Magnetic Fields, Phys. Rev. B. Condens. Matter, *55*, 1829 (1996).

3. D.-K. Seo, M.-H. Whangbo, B. W. Fravel, and L. K. Montgomery, "Comparison of the Fermi Surfaces of Isostructural Organic Conducting Salts (BEDT-TTF)$MHg(SCN)_4$ and $(BEDT\text{-}TSF)_2MHg(SCN)_4$ (M = NH_4 and K), Solid State Commun., *100*, 191 (1996).

4. L. K. Montgomery, T. Burgin, T. Miebach, D. Dunham, and J. C. Huffman, "Characterization of the Electrocrystallization Products of Bis(ethylenedithio)tetraselenafulvalene (BETS) and Tetrabutylammonium Tetrachlorogallate," Mol. Cryst. Liq. Cryst., *284*, 73 (1996).

5. L. K. Montgomery, T. Burgin, J. C. Huffman, J. Ren, M.-H. Whangbo, J. E. Schirber and D. L. Overmyer, "Characterization of the Organic Superconductor λ-$(BETS)_2GaCl_4$", Proceedings of the American Chemical Society Division of Polymeric Materials: Science and Engineering, *72*, 571 (1995).

6. T. Burgin, T. Miebach, J. C. Huffman, L. K. Montgomery, J. A. Paradis, C. Rovira, M.-H. Whangbo, S. N. Magonov, S. I. Khan, C. E. Strouse, D. L. Overmyer and J. E. Schirber, "20 K Crystal Structure, Electrical Transport, Electronic Band Structure, Scanning Tunnelling Microscopy and Pressure-RF Impedance Studies on the Organic Conducting Salt κ-$(BEDT\text{-}TSF)_2Cu[N(CN)_2]Br$," J. Mater. Chem., *5 (10)*, 1659 (1995).

7. Superconductivity, X-ray Structure and Electronic Band Structure of λ-$(BETS)_2GaCl_4$," Physica C, *219*, 490 (1994).

8. M. Chung, T. Burgin, E. Figueroa, Y.-K. Kuo, Y. Wang, L. K. Montgomery, and J. W. Brill, "Thermodynamics of the Anion Ordering Transitions in $(TMTSF)_2ReO_4$ and $(TMTSF)_2BF_4$," Phys. Rev. B.: Condens. Matter, *48*, 9256 (1993).

9. L.K. Montgomery, "Chemical Synthesis and Crystal Growth Techniques," in Organic Conductors: Fundamentals and Applications, Applied Physics Series, A.M. Hermann and J.P. Farges, Eds., Marcel Dekkar, New York, NY, Chapt. 4, 1994, p. 115.

10. L.K. Montgomery, T. Burgin, J.C. Huffman, K.D. Carlson, J.D. Dudek, G.A. Yaconi, L.A. Megna, P.R. Mobley, W.K. Kwok, J.M. Williams, J.E. Schirber, D.L. Overmyer, J. Ren, C. Rovira, and M.-H Whangbo, "The Synthesis and Characterization of Radical Cation Salts of Bis(ethylenedithio)tetraselenafulvalene," Synth. Met., *56*, 2090 (1993).

11. M. Chung, Y. Wang, J.W. Brill, T. Burgin, and L.K. Montgomery, "AC Calorimetry at CDW and SDW Transitions," Synth. Met., *56*, 2755 (1993).

12. Z.G. Xu, G. Minton, J.W. Brill, T. Burgin, and L.K. Montgomery, "Electric Field Dependence of Young's Modulus of $(TMTSF)_2PF_6$," Synth. Met., *56*, 2797 (1993).

ABSTRACT:

The principal objectives of this work were the design, synthesis, and preliminary characterization of new organic conductors and superconductors. Electrocrystallization facilities were constructed that accommodate 96 crystal growth cells. Crystal formation takes place in a temperature-controlled (±0.1 C), vibrationally-isolated, (vertical isolation efficiency at 10 Hz in 60-90%), inert-atmosphere environment. A variety of radical-cation salts of bis(ethylenedithio)tetraselenafulvalene were grown and characterized by crystallography, tight-binding band calculations, electronic transport, magnetic properties, and a number of other solid-state methods. Significant findings include the discovery of a tetrachlorogallate salt that is a superconductor with a transition temperature 5.5° higher than any previously known organic material containing selenium and magnetoresistance studies on mercury thiocyanate salts that suggest that strong electron-electron interactions are important in promoting and enhancing superconductivity in organic superconductors. A new organic conductor precursor, bis(ethylenedithio)tetrathiohaphthalene, was synthesized and several of its conducting salts were investigated in a preliminary manner. Numerous collaborative studies were undertaken.

Principal Investigator Annual Data Collection (PIADC) Survey Form

Please submit the requested data for the period 1 October 1994 through 30 June 1996 . Request you follow the data requirements and format instructions below. This data is due to your AFOSR program manager NLT 30 September 1994.

NOTE: If there is insufficient space on this survey to meet your data submissions, please submit additional data in the same format as identified below.

PI DATA

Name (Last, First, MI): Montgomery, Lawrence K.

Institution: Indiana University

Contract/Grant No. F49620-92-J-0534

AFOSR USE ONLY
Project/Subarea ____/____

NX ________

FY ________

NUMBER OF CONTRACT/GRANT CO-INVESTIGATORS

Faculty 1 Post Doctorates 1 Graduate Students 3 Other 1

PUBLICATIONS RELATED TO AFOREMENTIONED CONTRACT/GRANT

NOTE: List names in the following format: Last Name, First Name, MI

Include: Articles in peer reviewed publications, journals, book chapters, and editorships of books.

Do Not Include: Unreviewed proceedings and reports, abstracts, "Scientific American" type articles, or articles that are not primary reports of new data, and articles submitted or accepted for publication, but with a publication date outside the stated time frame.

Name of Journal, Book, etc.: Synthetic Metals
Title of Article: Synthesis and Preliminary Characterization of New Conducting Salts Derived from Bis(ethylenedithio)tetraselenafulvalene (BETS)
Author(s): L. K. Montgomery, B. W. Fravel, J. C. Huffman, C. C. Agosta, and S. A. Ivanov
Publisher (if applicable):
Volume: 85 **Page(s):** **Month Published:** **Year Published:** in press

Name of Journal, Book, etc.: Physical Review B, Condensed Matter
Title of Article: Electronic-Transport Studies of the Organic Metals α-$(BETS)_2NH_4Hg$-$(SCN)_4$ and α-$(BETS)_2KHg(SCN)_4$ in High Magnetic Fields
Author(s): S. A. Ivanov, C. H. Mielke, T. Coffey, D. A. Howe, C. C. Agosta, B. W. Fravel, and L. K. Montgomery
Publisher (if applicable):
Volume: 55 **Page(s):** 1829 **Month Published:** **Year Published:** 1996

Name of Journal, Book, etc.: Solid State Communications

Title of Article: Comparison of the Fermi Surfaces of Isostructural Organic Conducting Salts (BEDT-TTF)$MHg(SCN)_4$ and (BEDT-TSF)$_2MHg(SCN)_4$ ($M = NH_4$ and K)

Author(s): D.-K. Seo, M.-H. Whangbo, B. W. Fravel, and L. K. Montgomery

Publisher (if applicable):

Volume: 100 **Page(s):** 191 **Month Published:** **Year Published:** 1996

Name of Journal, Book, etc.: Molecular Crystals Liquid Crystals

Title of Article: Characterization of the Electrocrystallization Products of Bis(ethylenedithio)tetra-selenafulvalene (BETS) and Tetrabutylammonium Tetrachlorogallate

Author(s): L. K. Montgomery, T. Burgin, T. Miebach, D. Dunham, and J. C. Huffman

Publisher (if applicable):

Volume: 284 **Page(s):** 73 **Month Published:** **Year Published:** 1996

Name of Journal, Book, etc.: Proceedings of the American Chemical Society Division of Polymeric Materials: Science and Engineering

Title of Article: Characterization of the Organic Superconductor λ-(BETS)$_2GaCl_4$

Author(s): L. K. Montgomery, T. Burgin, J. C. Huffman, J. Ren, M.-H. Whangbo, J. E. Schirber and D. L. Overmyer

Publisher (if applicable):

Volume: 72 **Page(s):** 571 **Month Published:** **Year Published:** 1995

Name of Journal, Book, etc.: Journal of Materials Chemistry

Title of Article: 20 K Crystal Structure, Electrical Transport, Electronic Band Structure, Scanning Tunnelling Microscopy and Pressure-RF Impedance Studies on the Organic Conducting Salt κ-(BEDT-TSF)$_2Cu[N(CN)_2]Br$

Author(s): T. Burgin, T. Miebach, J. C. Huffman, L. K. Montgomery, J. A. Paradis, C. Rovira, M.-H. Whangbo, S. N. Magonov, S. I. Khan, C. E. Strouse, D. L. Overmyer and J. E. Schirber

Publisher (if applicable):

Volume: 5 (10) **Page(s):** 1659 **Month Published:** **Year Published:** 1995

AFOSR Technology Transfer/Transition Information for 1994

Directorate: Chemistry and Life Sciences
Program Manager:

Grant # or Lab Task #: No New Information

PI or Lab Task Manager :

PI telephone #:

Institution or AF Lab:

Address:

What is transitioned/transferred? (Biefly describe your basic research idea, result, theory, methodology, process, device, fact, knowledge, software etc., which significantly influences the direction of a customer's applied program in government, industry or academia):

Transitioned to whom (who is the customer?):
Name of applied program:

Organization (company, government agency, institution, etc):

Contact (person's name):

Telephone:

Date of transition (year, month or day):

Goal of applied program:

Purpose of transition (how is the direction of the relevant applied program changed by the transition):

8 Sept 94

HONORS/AWARDS RECEIVED DURING CONTRACT/GRANT LIFETIME

Include: All honors and awards received during the lifetime of the contract or grant, and any life achievement honors such as (Nobel prize, honorary doctorates, and society fellowships) prior to this contract or grant.

Do Not Include: Honors and awards unrelated to the scientific field covered by the contract/grant.

Honor/Award: No New Information Year Received: ______

Honor/Award Recipient(s): ______

Awarding Organization: ______